Biodiesel Production in Fixed-Bed Catalytic Reactors

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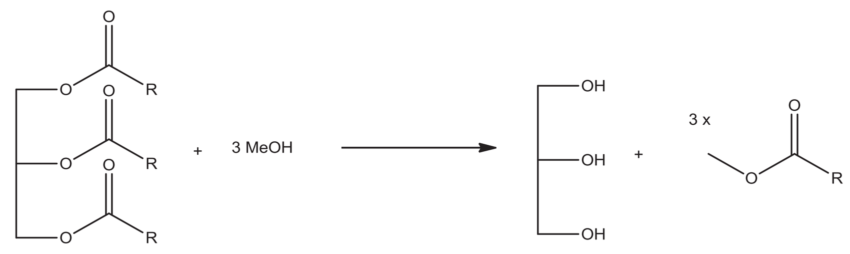
Introduction to biodiesel

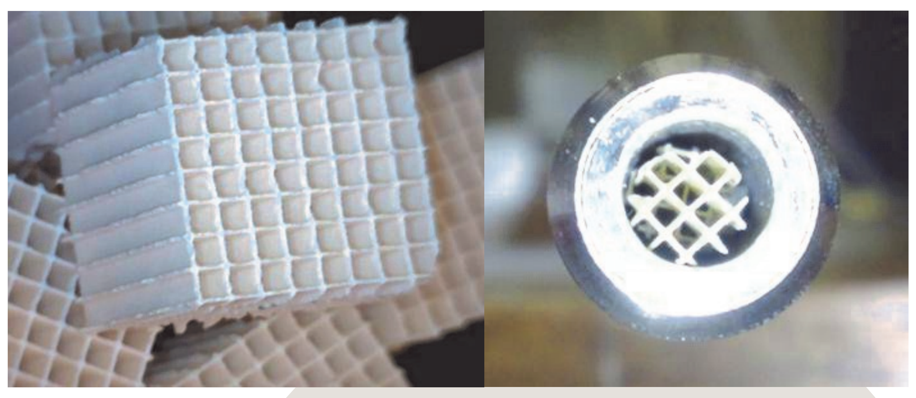
Biodiesel is a potentially renewable fuel made by the transesterification of vegetable oils or animal fats with a primary alcohol; in this case methanol is used to make fatty acid methyl esters, or FAME. This can be performed with an acid or base catalyst. As a fuel, biodiesel can be interchanged directly with conventional diesel, and so can be used with the existing infrastructure. Environmental advantages include biodegradability and reduced emissions of volatile organics, carbon monoxide, and particulates[1]. This project aims to develop a continuous reactor with a catalyst supported on a monolith structure.



General reaction scheme for the transesterification of triglyceride with methanol.

Monoliths

Monoliths are catalyst support structures forming a continuous series of regular channels. These may be coated with additional support material, such as alumina, along with a catalyst. The monoliths used in this project are thin walled cordierite with parallel channels.

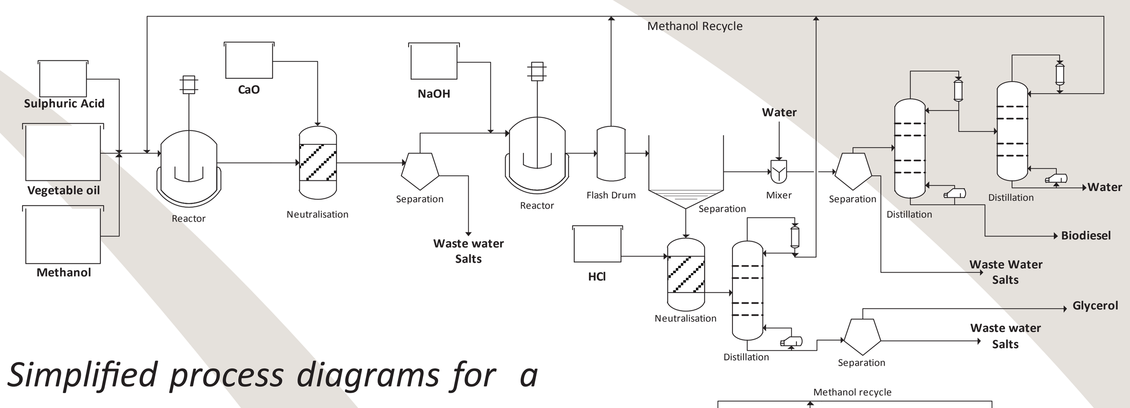


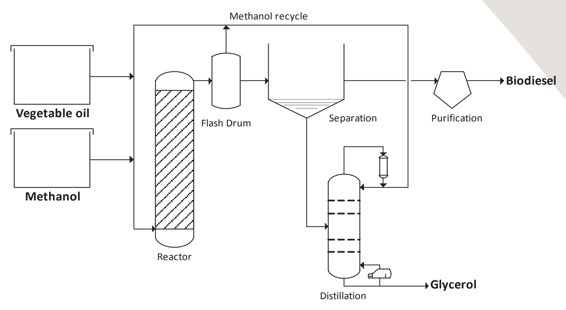
Cordierite monoliths, left, and monoliths loaded into the continuous reactor, right

Why heterogeneous catalysis?

Ideally, if a robust and impurity tolerant heterogeneous catalyst can be found, this will reduce:

- Plant equipment and footprint
- Feedstocks (catalysts, neutralising agents)
- Waste water and salts

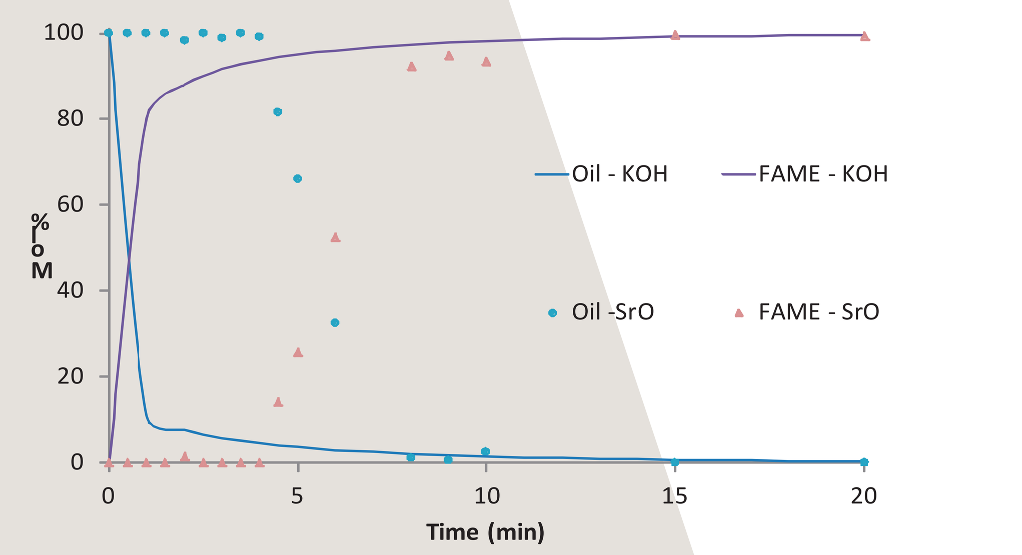




Simplified process diagrams for a typical homogeneous biodiesel production process, above, and an ideal heterogeneous production process, right. Adapted from literature[2,3].

Strontium oxide as a catalyst

Strontium oxide is an effective solid catalyst for transesterification. SrO powder was used to transesterify rapeseed oil, and the data was compared with literature data for potassium hydroxide[4], a typical catalyst for homogeneous biodiesel production. After an initial delay, SrO powder shows a similar rate to KOH.

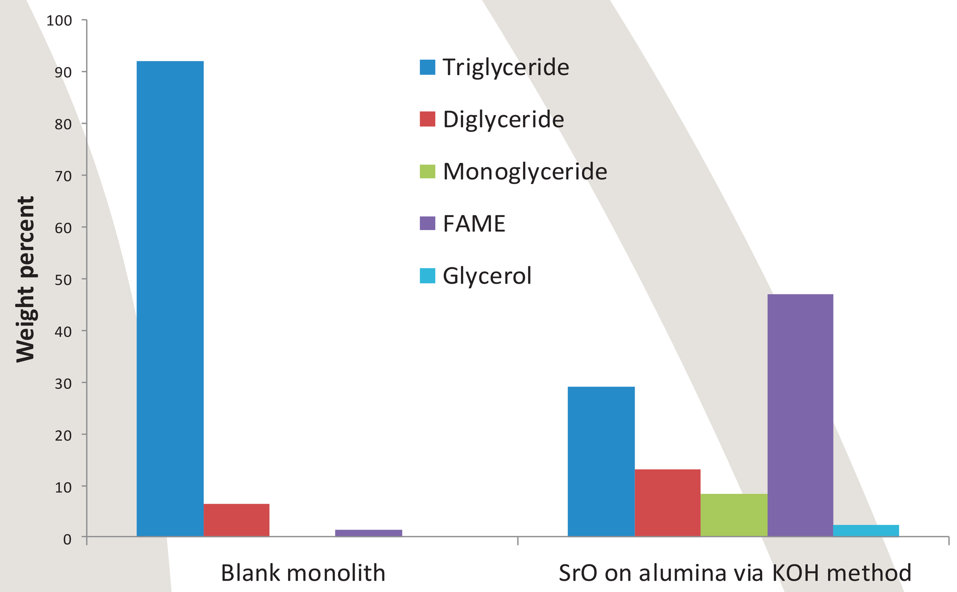


Comparison of SrO catalysed reaction and data for homogeneous KOH reaction from the literature (both 1.5 wt% catalyst w.r.t. oil, 65°C)

Coating method

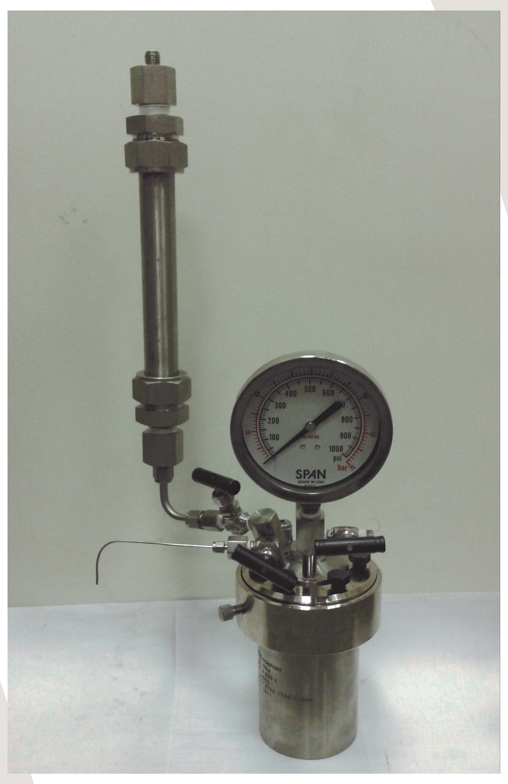
The main catalyst of interest is strontium oxide. This has been shown to be a very effective heterogeneous catalyst for transesterification. The monoliths are cut to size and before being coated. Currently , the most successful method is coating with strontium nitrate, reacting this with potassium hydroxide to get strontium hydroxide, then calcining at 720°C under nitrogen.

Cutting → **Coating** → **Calcining** → **Catalysis**



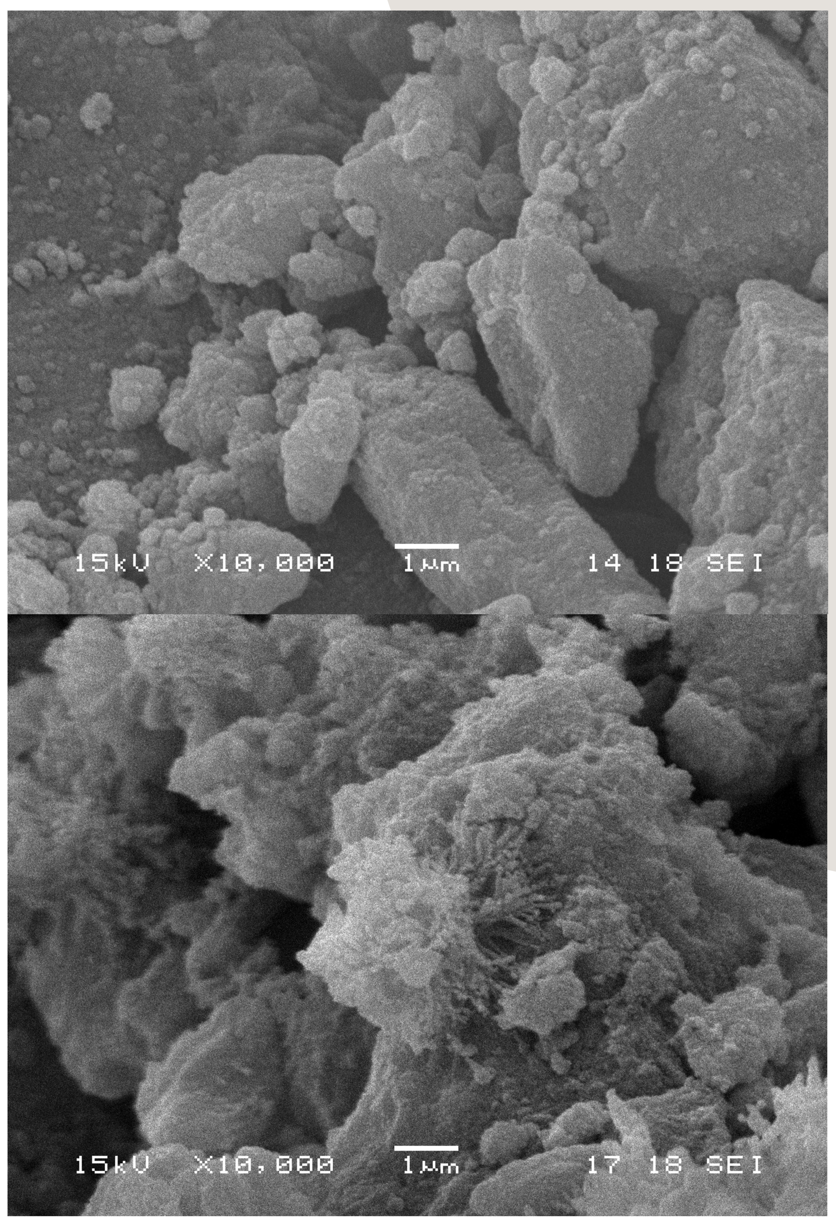
Conversion of vegetable oil to FAME after 24 hours. SrO loading w.r.t. oil is 0.08% (c.f. 1.5% for typical reaction)

Testing the catalysts



Monolithic catalysts are tested at 120°C in a stainless steel autoclave, with a 6:1 molar ratio of methanol:oil. Samples are taken regularly and analysed by gas chromatography. The results from the most promising candidate are shown in the chart to the left.

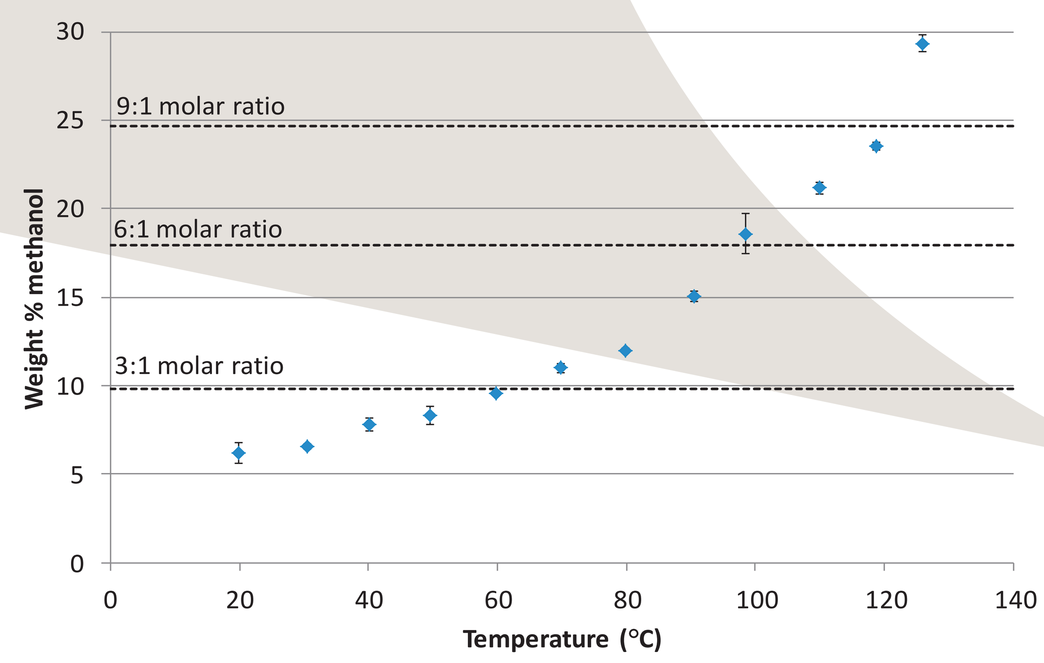
Steel reaction vessel for testing potential catalysts. The vertical cylinder can be filled with methanol for pressurised injection to control the starting point of the reaction.



SEM images of unloaded alumina coated monolith, top, and SrO loaded alumina monolith, bottom

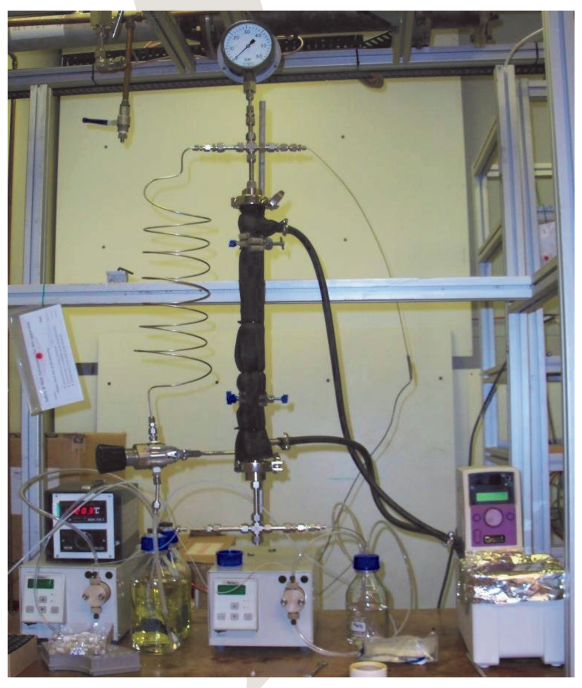
Solubility: Is it single-phase?

If the oil and methanol are miscible this will improve mass transfer and simplify reactor design. Methanol and oil were mixed in a glass pressure vessel at a range of temperatures, and after the phases were separated samples were taken from the oil phase. While the stoichiometry requires a 3:1 methanol:oil ratio, reactions are generally carried out between 6:1 and 9:1 to push the reaction to completion.



Methanol solubility in oil with temperature

Conclusions and future work



Continuous reactor for testing monolithic catalysts, capable of pressures up to 20 bar

- Strontium oxide is a promising heterogeneous catalyst
- A coating method has been developed to deposit SrO on a monolithic support
- Catalyst candidates have been tested in a batch reactor
- The methanol-oil mixture is single phase at reaction conditions

Future work:

- Catalysts will be tested in a continuous reactor
- Continuous reaction data will be used to test a set of reaction modelling equations that have been developed

[1] Bannister, C.D., *et al.*, *Proc. Inst. Mech. Eng.* D J. Automob. Eng., **2010**, *224*, 405-421. [2] Melero, J. A. *et al.*, *Green Chem.* **2009**, *11*, 1285-1308. [3] Helwani, J. *et al.*, *J. Fuel Process. Technol.* **2009**, *90*, 1502-1514. [4] Vicente, G. *et al.*, *Ind. Eng. Chem.* Res. **2005**, *44*, 5447-5454

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